

# PATENT SPECIFICATION

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## (54) IMPROVEMENTS IN OR RELATING TO THE PREPARATION OF DISPERSIBLE DISPERSION POWDERS

(71) We, HOECHST AKTIENGESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:-

The invention relates to the preparation of dispersible vinyl acetate copolymer dispersion powders and the use thereof in the field of coating and building.

Polyvinyl acetate homo- and co-polymer dispersion powders dispersible with water are known. Homopolymer dispersion powders are used chiefly in the adhesive field and copolymer dispersion powders are used chiefly in the coating and building field. In addition to the general requirements of a dispersion powder, such as good storage stability, good running capacity and good dispersibility in water, there are further, special requirements for use in the coating and building field. Thus, dispersions obtained with dispersion powders with water should preferably have a minimum film-forming temperature of about 0°C, and the polymers should have a good stability to alkali. In combination with binding agents that set hydraulically, dispersion powders should have a good compatibility and bring about an improvement in the flexural strength and compression strength of test bodies. When used as the sole binding agents in the so-called synthetic resin-bound plasters for coating surfaces such, for example, as asbestos cement, wood and masonry, they must give an especially high adhesion and abrasion resistance on all substrata, especially in the wet state.

DAS 1,719,317 describes a process for producing non-clogging dispersible powders from polymerisates and copolymerisates of vinyl acetate by the spray drying of dispersions. The dispersions are prepared using polyvinyl alcohols as protective colloids, 0.5 to 4 parts by weight of polyvinyl alcohol having a viscosity of 3 to 13 cP and a degree of hydrolysis of 75 to 95 mol-%, being added at an 80-90% monomer conversion. However, the dispersion powders produced by DAS 1,719,317 do not fulfil the conditions required for producing sufficiently waterproof synthetic resin-bound plasters.

DOS 2,214,410 describes a process for the production of a re-dispersible vinyl acetate/ethylene polymer dispersion powder by spray drying a vinyl acetate/ethylene polymer dispersion. The dispersions are prepared at ethylene pressures of up to 100 atmospheres and polymerisation temperatures of preferably 50 to 70°C using small quantities of ionic emulsifiers and polyvinyl alcohol as a protective colloid. The synthetic resin plasters prepared with these dispersion powders have a good waterproof character. However, for vinyl acetate/ethylene dispersions, polymerisation temperatures above 70°C are desired, because then the dispersions can be prepared more economically with shorter monomer-dosing times, but the synthetic resin-bound plasters prepared with the dispersion powders obtained at such temperatures have not been sufficiently waterproof.

The present invention provides a process for the preparation of a dispersion powder dispersible in water and suitable as binding agent for synthetic resin-bound plasters, which comprises the emulsion polymerisation of vinyl acetate with one or more other olefinically unsaturated monomers in the presence of

- (a) 0.02 to 1.0% by weight of ionic emulsifier, calculated on the copolymer,  
 (b) 0.05 to 2.0% by weight of a polyethoxylated non-ionic emulsifier, calculated on the copolymer.

- (c) 2.5 to 20% by weight, calculated on the copolymer, of at least one polyvinyl alcohol of which an aqueous solution of 4% strength has at 20°C a viscosity of 3 to 45 mPas and which has an ester number of 90 to 215 mg of KOH/g, and

- 5 (d) a radical initiator,  
at a polymerisation temperature in the range of from 70 to 100°C, adding more  
polyvinyl alcohol specified under (c) where appropriate so that the content thereof in  
the copolymer dispersion obtained is from 5 to 20% by weight calculated on the  
copolymer, and spray drying in a spray drying tower to form a fine powder with the  
10 simultaneous, but spatially separated, introduction of anti-caking agent having an  
average particle size of the primary particles of 0.01 to 0.5µ, preferably in an amount  
in the range of from 2 to 20% by weight, calculated on the content of solid matter of  
the aqueous dispersion. 10

The copolymer preferably has a vinyl acetate content exceeding 40% by weight. Other  
olefinically unsaturated monomers suitable as copolymer components are, for example,  
15 vinyl esters of straight-chained and branched carboxylic acids having 3 to 18 carbon atoms,  
acrylic, methacrylic, maleic and fumaric acid esters of aliphatic alcohols having 1 to 18  
carbon atoms, vinyl chloride, ethylene, isobutylene and higher α-olefins having 4 to 12  
carbon atoms. Suitable monomer combinations are, for example, vinyl acetate/2-  
ethylhexanoic acid vinyl ester, vinyl acetate/vinyl laurate, vinyl acetate/vinyl ester of  
20 carboxylic acids branched in the α-position and having 10 carbon atoms, vinyl acetate/  
ethylene, vinyl acetate/vinyl pivalate/ethylene and vinyl acetate/vinyl chloride/ethylene. 20

Preferably, the monomer combination is such that the dispersion formed has a minimum  
film-forming temperature of about 0°C. However, there may also be used monomer  
combinations which lead to dispersions having a minimum film-forming temperature above  
25 0°C in which case a reduction to about 0°C may be achieved by the addition of one or more  
external plasticisers, for example adipic and phthalic acid esters, trialkyl- and triaryl-  
phosphoric acid esters or glycerine esters of long-chained carboxylic acids. In addition to  
the monomers mentioned above, other monomers having a stabilising action on the  
dispersion may also be used, preferably in a concentration of up to 5% by weight calculated  
30 on the total polymer. Such monomers are, for example, sodium vinyl sulphonate,  
monomers containing carboxyl groups, for example acrylic, methacrylic, crotonic and  
itaconic acid and monoesters of maleic acid, of which the alcohol components preferably  
contain 1 to 18 carbon atoms, and acrylamide and methacrylamide. In addition,  
35 components having a cross-linking action, for example compounds containing methylol  
groups, e.g. N-methylol-acrylamide or monomers containing two or more unsaturated  
double bonds, e.g. diallyl maleate, tetraallyloxyethane or adipic acid divinyl ester, may also  
be used. 35

The emulsifier/protective colloid system which yields the vinyl acetate copolymer  
dispersion powder of the present invention, is composed of ionic and non-ionic emulsifiers  
40 and at least one polyvinyl alcohol as protective colloid. 40

The ionic emulsifier component is preferably used in an amount of 0.05 to 1% by weight,  
more especially 0.05 to 0.5% by weight, calculated on the polymer. Preferred emulsifiers of  
this type are alkyl sulphates having from 10 to 16 carbon atoms.

45 The non-ionic polyethoxylated emulsifier component is preferably used in an amount of  
0.1 to 2% by weight, more especially 0.1 to 1% by weight, calculated on the polymer. 45  
Preferred emulsifiers of this type are polyethoxylated alcohols, preferably aliphatic  
alcohols, polyethoxylated alkyl-phenols and polyethoxylated polypropylene glycols.

The polyvinyl alcohol component is used in preparing the powder in an amount of 5 to  
20% by weight, preferably 7 to 15% by weight, calculated on the polymer, and should have  
50 an ester number of 90 to 215 mg of KOH/g, preferably 90 to 160 mg of KOH/g, and an  
aqueous solution thereof of 4% strength should have a viscosity at 20°C of 3 to 45 mPas,  
preferably 4 to 20 mPas. For preparing the dispersion powder of the invention, the  
polymerisation liquor may contain, at the beginning of the preparation of the dispersion, all  
the polyvinyl alcohol used in the process, i.e. 5 to 20% by weight, calculated on the  
55 copolymer, or, advantageously, 50 to 90% by weight of the polyvinyl alcohol used (2.5 to  
18% by weight of the copolymer), and the remaining 50 to 10% by weight is added  
subsequently in the form of an aqueous solution to the finished dispersion. 55

Advantageously the pH of the dispersion liquor is adjusted to a value within the range of  
from 4 to 7.5. A suitable buffer such, for example, as sodium acetate, sodium phosphate or  
60 sodium bicarbonate, may be added to the dispersion liquor to control the pH. 60

The emulsifier/protective colloid system permits using the especially advantageous  
polymerisation temperatures of 70 to 100°C. The higher the polymerisation temperature,  
the more economical is the process as the heat of polymerisation can be more easily  
abstracted at higher polymerisation temperatures and in this way the period during which  
65 monomer is supplied and therewith the whole period of preparation of the dispersion can be 65

shortened.

The polymerisation may be initiated by a conventional radical initiator, preferably a water-soluble per compound, although a monomer-soluble compound may also be used.

5 The vinyl acetate-copolymerisable dispersion usually has a content of solid matter in the range of from 30 to 60% by weight. After polymerisation has ended, the content of solid matter may be adjusted to a value favourable for spray drying, for example 30 to 45% by weight, for example by the addition of water or an aqueous solution of polyvinyl alcohol. 5

10 A dispersion powder of the present invention is prepared from the aqueous synthetic resin dispersion by spray drying with the simultaneous, but spacially separated, introduction of anti-caking agent having an average particle size of the primary particles in the range of from 0.01 to 0.5  $\mu$ , and, if appropriate, with the addition of more polyvinyl alcohol of which an aqueous solution of 4% strength has at 20°C a viscosity of 3 to 45 mPas and which has an ester number of 90 to 215 mg of KOH/g, so that the content thereof in the copolymer dispersion is from 5 to 20% by weight calculated on the copolymer. 10

15 Suitable anti-caking agents are, for example, aluminium silicates, calcium carbonates or silicic acids, having an average particle size of the primary particles in the range of from 0.01 to 0.5  $\mu$ . Especially preferred anti-caking agents are silicic acids and aluminium silicates, and advantageous quantities are 2 to 20% by weight calculated on the content of solid matter in the aqueous dispersion (total of emulsifiers, polyvinyl alcohol, initiator, anti-caking agent and copolymer). The anti-caking agent is introduced into the spray drying tower simultaneously with, but separately from, the aqueous dispersion. This method of supplying the anti-caking agent prevents to a great extent the formation of undesired coatings on the wall of the drier. 15

25 Dispersion powders prepared in accordance with the invention have a good stability to storage, and run well and can be stirred with water to form rapidly homogeneous dispersions of stable viscosity that are stable to storage. They are well suited for the production of adhesives, sizes and coating preparations. They are outstandingly useful for the production of synthetic resin-bound plasters in dry form. These synthetic resin-bound plasters may be prepared in the dry state by intimately mixing various granulated mineral additives with the vinyl acetate copolymerisation powders of the invention. At the place of use these dry powders are stirred with water and applied in a suitable manner to a wall or masonry. After drying these synthetic resin-bound plasters fulfil to a high degree the necessary requirements, such as a good wet and dry adhesive power and good resistance to water. 25

30 The following Examples illustrate the invention. 30

#### Example 1

1. The production of a vinyl acetate/ethylene copolymer dispersion.

40 A solution of 7 parts by weight of sodium lauryl sulphate, 76 parts by weight of polyethoxylated nonyl-phenol containing 30 mol ethylene oxide/mol nonyl-phenol, 680 parts by weight of polyvinyl alcohol (of which a 4% aqueous solution had a viscosity at 20°C of about 8 mPas and which had an ester number of 140 mg per KOH/g), 45 139 parts by weight of polyvinyl alcohol (of which a 4% aqueous solution had a viscosity at 20°C of about 18 mPas and which had an ester number of 140 mg of KOH/g), 15.3 parts by weight of anhydrous sodium acetate, and 7700 parts by weight of water, adjusted to a pH of 6.0, was introduced into a pressure reaction vessel having a capacity of 50 30 parts by volume and provided with a temperature regulating device and stirring means. The reactor was flushed with nitrogen and ethylene to remove practically all the oxygen. The stirring means was then set at 150 revolutions per minute, 760 parts by weight of vinyl acetate were added to the mixture and the contents of the vessel were heated to 60°C. A solution of 6 parts by weight of ammonium persulphate in 500 parts by weight of water was 55 added at 60°C and the contents of the vessel were further heated to 80°C. During the heating-up process, ethylene was introduced up to a pressure of 20 bar. When an internal temperature of 80°C was reached, the introduction of 6880 parts by weight of vinyl acetate and a solution of 4.2 parts by weight of ammonium persulphate in 350 parts by weight of water at an internal temperature of 80°C and an ethylene pressure of 20 bar was begun and 60 continued over a period of 5 hours. When the introduction was complete a solution of 1.8 parts by weight of ammonium persulphate in 150 parts by weight of water, was added to the mixture and the whole was further heated for 1.5 hour at an external temperature of 85°C. The supply of ethylene was then cut off and the dispersion was cooled to room temperature. A solution of 220 parts by weight of polyvinyl alcohol (of which a 4% aqueous solution had 65 a viscosity at 20°C of about 4 mPas and which had an ester number of 140 mg of KOH/g) in 65

1280 parts by weight of water, was then added to the dispersion. The vinyl acetate/ethylene copolymer dispersion of 50% strength was then drawn off; it had an ethylene content of about 14% by weight, a residual monomer content of less than 0.5% by weight, a latex viscosity (Epprecht rheometer C/II) of 1.5 mPas and a minimum film-forming temperature below 0°C.

2. The production of the vinyl acetate/ethylene copolymer powder.

The vinyl acetate/ethylene copolymer dispersion prepared in Example I. 1 was diluted with water to a content of solid matter of 40% by weight, and spray dried in an atomising tower, of which the cylindrical part had a diameter of 1.6 m and a length of 4 m and of which the conical part had a length of 2 m. The dispersion was supplied by means of an eccentric screw pump to a two-component atomising nozzle having a product bore 3 mm in diameter. The drying was carried out in parallel flow, and as the drying gas there was used nitrogen having a throughput of 750 m<sup>3</sup>/h. The temperature of the drying gas at the inlet of the tower was 115°C and in the cyclone separator 65°C. The throughput of atomising air for the product nozzle was 70 parts by weight at a pressure in front of the nozzle of 5 bar and a temperature of 23°C. Simultaneously with the introduction of the dispersion, a finely divided powder of silicic acid having an SiO<sub>2</sub> content of 93%, a surface area according to BET of 250 m<sup>2</sup>/g and an average size of the primary particles of 0.018 μ, was introduced as an anti-caking agent in an amount of 5%, calculated on the content of solid matter of the aqueous dispersion, into the spraying tower through a second two-component nozzle situated in the vicinity of the wall of the tower only a little below the product nozzle.

The dispersion powder so obtained had a good running capacity and a good stability to storage, that is to say, a sample of the powder even after being stored for 24 hours at 50°C under a load of 200 g/cm<sup>2</sup> could easily be loosened up. The apparent density of the powder was 380 g/l, the volume after shaking was 81% and the compression density was 470 g/l. The powder could easily be stirred with water to form a stable dispersion, of which the viscosity, measured with a dispersion of 50% strength and according to Epprecht/measuring system C 2, was 7.3 Pas.

3. The use of the vinyl acetate/ethylene copolymer powder.

In addition to its suitability for preparing sizes, adhesives and coating preparations the above powder could be used as the sole binding agent for the production of synthetic resin dry plasters having excellent properties. A selection of various recipes for the production of synthetic resin plasters is given in the accompanying Table.

The preparation of the plasters was carried out by intense mixing of the solid constituents, then adding water, again thoroughly mixing and applying the plasters with a wiper or trowel to test plates of asbestos cement having a thickness of about 5 mm. The dried out plasters were distinguished by a very good resistance to water and a very good adhesive power on the underlying material. After storing the plates in water the plasters remained practically unaffected. Their adhesion to asbestos cement was very good and detrition in the wet state was insignificant.



Comparative Example I (No non-ionic polyethoxylated emulsifier & low polymerisation temperature).

5 A vinyl acetate/ethylene copolymer dispersion was prepared at an ethylene pressure of 20 bar in accordance with the procedure given in Example I except that the polymerisation temperature was 60°C. and the polymerisation liquor contained no polyethoxylated nonyl-phenol. Owing to the low polymerisation temperature of 60°C. and the difficulty connected therewith in abstracting the heat of polymerisation, the period of introducing the monomers had to be extended from 5 to 8 hours.

10 The vinyl acetate/ethylene copolymer dispersion of 50% strength so obtained could be spray dried, as in Example I, in the presence of the anti-caking agent described therein to form a dispersion powder stable to storage, which is also suitable for the production of synthetic resin-bound plasters having a good waterproof character.

15 Comparative Example II (No non-ionic polyethoxylated emulsifier).

The procedure for preparing the vinyl acetate/ethylene copolymer dispersion was the same as in Comparison Example I, except that the desirably high polymerisation temperature of 80°C was used as in Example I. The period of introduction of the monomers was 5 hours as in Example I.

20 The vinyl acetate/ethylene copolymer dispersion so obtained was spray-dried by the procedure given in Example I in the presence of the anti-caking agent, silicic acid, to form a dispersion powder, which was worked up according to the directions given in Example I to form synthetic resin-bound plasters, but these were insufficiently waterproof and had a poor wet adhesive power on asbestos cement. After storing the through-dried plaster in water, the plaster could easily be separated from the underlying material and in the surface it could be easily rubbed off.

25 The comparative Examples I and II make clear that low polymerisation temperature, (which leads to unavoidably long and economically unfavourable periods of polymerisation), the use of the emulsifier/protective colloid system in accordance with the invention is not essential for the production of waterproof synthetic resin plasters. However, at the economically favourable high polymerisation temperatures, the desired aim can be achieved only by the use of the emulsifier/protection colloid system of the invention.

#### Example II

35 A vinyl acetate copolymer dispersion was prepared in a polymerisation vessel having a capacity of 100 parts by volume, provided with a horseshoe mixer and reflux condenser, from a monomer mixture of

18,000 parts by weight of vinyl acetate and  
12,000 parts by weight of a vinyl ester of carboxylic acids having 10 carbon atoms and branched in the  $\alpha$ -position,  
40 in a polymerisation liquor containing

30,800 parts by weight of water,  
2,700 parts by weight of polyvinyl alcohol (of which a 4% aqueous solution had a viscosity at 20°C of 8 mPas and which had an ester number of 140 mg of KOH/g),  
45 150 parts by weight of polyethoxylated polypropylene glycol having a molecular weight of about 2000 and an ethylene oxide content of about 40% by weight,

24 parts by weight of sodium lauryl sulphate, and  
60 parts by weight of anhydrous sodium acetate, using a catalyst solution containing  
45 parts by weight of ammonium persulphate, and  
800 parts by weight of water.

50 at a polymerisation temperature of 80°C and a period of introduction of the monomers of 2.5 hours. After the preparation, 990 parts by weight of phthalic acid dibutyl ester and a solution of 750 parts by weight of polyvinyl alcohol (of which a 4% aqueous solution had a viscosity at 20°C of 4 mPas and which had an ester number of 140 mg of KOH/g in 3000 parts by weight of water) was added to the dispersion.

55 The vinyl acetate copolymer dispersion of about 50% strength so obtained had a minimum film-forming temperature of 0°C and a latex viscosity measured in the Epprecht-rheometer C/2 of 2.5 Pas.

60 The spray drying of the dispersion, diluted with water to a content of solid matter of 40% by weight, was carried out according to the data given in Example I.2 with 8%, calculated on the content of solid matter in the dispersion, of synthetic silicic acid as anti-caking agent having an SiO<sub>2</sub>-content of 93%, a surface area according to BET of 230 M<sup>2</sup>/g and an average size of the primary particles of 0.018  $\mu$ .

This resulted in a flowable dispersion powder having good storage stability and which was outstandingly suitable for the production of waterproof plasters.

*Example III*

A vinyl acetate/vinyl chloride/ethylene terpolymer dispersion was prepared at a polymerisation temperature of 80°C according to the procedure given in Example I. 1 except that the ethylene pressure was 45 bar and there were used, instead of 7640 parts by weight of vinyl acetate, a mixture of 5350 parts by weight of vinyl acetate and 2290 parts by weight of vinyl chloride, and, instead of 76 parts by weight of polyethoxylated nonyl-phenol, 57 parts by weight of polyethoxylated stearyl alcohol containing 20 mol of ethylene oxide per mol of stearyl alcohol.

The vinyl acetate/vinyl chloride/ethylene terpolymer dispersion, after dilution to a content of solid matter of 40% by weight, was spray dried in accordance with the prescription given in Example I.2 to form a flowable dispersion powder stable to storage, which by using the recipes formulated in the Table was outstandingly suitable for the production of waterproof synthetic resin plasters.

*Example IV*

A vinyl acetate/2-ethylhexanoic acid vinyl ester copolymer dispersion was prepared in accordance with the procedure given in Example II except that, instead of the monomer mixture given in Example II, a mixture of 21000 parts by weight of vinyl acetate and 9000 parts by weight of 2-ethylhexanoic acid vinyl ester, was used and no phthalic acid dibutyl ester was subsequently added to the dispersion.

The dispersion could be spray dried, as described in Example II, to form a flowable dispersion powder stable to storage, which was outstandingly suitable for the production of waterproof synthetic resin plasters.

*Example V*

A vinyl acetate/dibutyl maleate copolymer dispersion was prepared in accordance with the prescription given in Example II, except that, instead of the monomer mixture given in Example II, a mixture of 20,100 parts by weight of vinyl acetate and 9900 parts by weight of dibutyl maleate was used, and, instead of the polyethoxylated polypropylene glycol used in Example II, one having an ethylene oxide content of 20% by weight.

The dispersion powder obtained from this dispersion by spray drying was also outstandingly suitable for the production of waterproof synthetic resin plasters.

## WHAT WE CLAIM IS:

1. A process for the preparation of a dispersion powder dispersible in water and suitable as binding agent for synthetic resin-bound plasters, which comprises the emulsion polymerisation of vinyl acetate with one or more other olefinically unsaturated monomers in the presence of
  - (a) 0.02 to 1.0% by weight of ionic emulsifier, calculated on the copolymer,
  - (b) 0.05 to 2.0% by weight of a polyethoxylated non-ionic emulsifier, calculated on the copolymer,
  - (c) 2.5 to 20% by weight, calculated on the copolymer, of at least one polyvinyl alcohol of which an aqueous solution of 4% strength has at 20°C a viscosity of 3 to 45 mPas and which has an ester number of 90 to 215 mg of KOH/g, and
  - (d) a radical initiator,
 at a polymerisation temperature in the range of from 70 to 100°C, adding more polyvinyl alcohol specified under (c) where appropriate so that the content thereof in the copolymer dispersion obtained is from 5 to 20% by weight calculated on the copolymer, and spray drying in a spray drying tower to form a fine powder with the simultaneous, but spatially separated, introduction of anti-caking agent having an average particle size of the primary particles in the range of from 0.01 to 0.5  $\mu$ .
2. A process as claimed in claim 1, wherein all the polyvinyl alcohol used is present during the emulsion polymerisation.
3. A process as claimed in claim 1, wherein 50 to 90% of the amount of total polyvinyl alcohol used is present during the emulsion polymerisation.
4. A process as claimed in any one of claims 1 to 3, wherein the non-ionic polyethoxylated emulsifier is a polyethoxylated alkyl-phenol, polyethoxylated alcohol or polyethoxylated polypropyl glycol.
5. A process as claimed in any one of claims 1 to 4, wherein the ionic emulsifier is an alkyl sulphate having from 10 to 16 carbon atoms.
6. A process as claimed in any one of claims 1 to 5, wherein the polyvinyl alcohol has an ester number of from 90 to 160 mg KOH/g and a 4% solution thereof has a viscosity at 20°C of from 4 to 20 mPas.
7. A process as claimed in any one of claims 1 to 6, wherein the non-ionic emulsifier is present in an amount of from 0.1 to 2% by weight, calculated on the copolymer.
8. A process as claimed in any one of claims 1 to 7, wherein the non-ionic emulsifier is

- present in an amount of from 0.1 to 1% by weight, calculated on the copolymer.
9. A process as claimed in any one of claims 1 to 8, wherein the ionic emulsifier is present in an amount of from 0.05 to 1% by weight, calculated on the copolymer.
10. A process as claimed in any one of claims 1 to 9, wherein the ionic emulsifier is present in an amount of from 0.05 to 0.5% by weight, calculated on the copolymer.
11. A process as claimed in any one of claims 1 to 10, wherein the total polyvinyl alcohol used is from 7 to 15% by weight, calculated on the copolymer.
12. A process as claimed in any one of claims 1 to 11, wherein the copolymer is derived from
- (i) a vinyl ester of a carboxylic acid having from 3 to 18 carbon atoms, acrylic, methacrylic, maleic or fumaric acid ester of an aliphatic alcohol having from 1 to 18 carbon atoms, vinyl chloride, ethylene, isobutylene or an  $\alpha$ -olefin having from 4 to 12 carbon atoms, or a mixture of two or more such monomers, and
- (ii) vinyl acetate.
13. A process as claimed in claim 8, wherein the copolymer is derived from vinyl acetate and 2-ethylhexanoic acid vinyl ester; vinyl acetate and vinyl laurate; vinyl acetate and vinyl ester of a carboxylic acid having 10 carbon atoms and branched in the  $\alpha$ -position;
- vinyl acetate and ethylene;
- vinyl acetate, vinyl prvalate and ethylene, or
- vinyl acetate, vinyl chloride and ethylene.
14. A process as claimed in any one of claims 1 to 13, wherein the vinyl acetate content of the copolymer is more than 40% by weight.
15. A process as claimed in any one of claims 1 to 14, wherein the dispersion has a minimum film-forming temperature of substantially 0°C.
16. A process as claimed in any one of claims 1 to 14, wherein the dispersion contains a plasticiser.
17. A process as claimed in any one of claims 1 to 16, wherein the polymerisation is carried out in the presence of a stabiliser or cross-linking monomer.
18. A process as claimed in any one of claims 1 to 17, wherein the dispersion has a pH in the range of from 4 to 7.5.
19. A process as claimed in claim 1, wherein polymerisation is carried out substantially as described in any one of Examples I, II, III, IV and V herein.
20. A process as claimed in any one of claims 1 to 19, wherein before spray drying the solid matter content of the copolymer dispersion is adjusted to 30 to 45% by weight.
21. A process as claimed in any one of claims 1 to 20, wherein the anti-caking agent is aluminium silicate, calcium carbonate or silicic acid.
22. A process as claimed in any one of claims 1 to 21, wherein the anti-caking agent is used in an amount of from 2 to 20% by weight, calculated on the total solid water in the dispersion.
23. A process as claimed in claim 1, which is carried out substantially as described in any one of Examples I, II, III, IV and V herein.
24. A dispersion powder dispersible in water and suitable as binding agent for synthetic resin-bound plasters, whenever prepared by a process as claimed in any one of claims 1 to 23.
25. A process for the preparation of a copolymer dispersion which comprises the emulsion polymerisation at a temperature in the range of from 70 to 100°C of vinyl acetate with one or more other olefinically unsaturated monomers in the presence of
- (a) 0.02 to 1.0% by weight of ionic emulsifier, calculated on the copolymer,
- (b) 0.05 to 2.0% by weight of a polyethoxylated non-ionic emulsifier, calculated on the copolymer,
- (c) 2.5 to 20% by weight, calculated on the copolymer, of at least one polyvinyl alcohol of which an aqueous solution of 4% strength has at 20°C a viscosity of 3 to 45 mPas and which has an ester number of 90 to 215 mg of KOH/g, and
- (d) a radical initiator.
- and adding more polyvinyl alcohol specified under (c) where appropriate so that the content thereof in the copolymer dispersion obtained is from 5 to 20% by weight calculated on the copolymer.
26. A copolymer dispersion, whenever prepared by a process as claimed in claim 25.
27. A process for the preparation of a dispersion powder dispersible in water and suitable as binding agent for synthetic resin-bound plasters, which comprises spray drying a copolymer dispersion as claimed in claim 26 with the simultaneous, but spacially separated, introduction of anti-caking agent having an average particle size of the primary particles in the range of from 0.01 to 0.5  $\mu$ , and, if appropriate, with the addition of more polyvinyl



alcohol of which an aqueous solution of 4% strength has at 20°C a viscosity of 3 to 45 mPas and which has an ester number of 90 to 215 mg of KOH/g. so that the content thereof in the copolymer dispersion is from 5 to 20% by weight calculated on the copolymer.

28. A dispersion powder dispersible in water and suitable as binding agent for synthetic resin-bound plasters, whenever prepared by a process as claimed in claim 27.
29. An emulsion/protective colloid system for emulsion copolymerisation, which comprises
  - a) from 0.02 to 1 part by weight of ionic emulsifier,
  - b) from 0.05 to 2 parts by weight of a polyethoxylated non-ionic emulsifier, and
  - c) from 2.5 to 20 parts by weight of at least one polyvinyl alcohol of which an aqueous solution of 4% strength has at 20°C a viscosity of 3 to 45 mPas and which has an ester number of 90 to 215 mg KOH/g.
30. An emulsion/protective colloid system as claimed in claim 29, wherein the amount of polyvinyl alcohol is from 5 to 20 parts by weight.
31. A composition which comprises a dispersing powder as claimed in claim 24 or claim 28 and a binding agent that sets hydraulically.
32. A synthetic resin-bound plaster composition in which the binding agent is a dispersion powder as claimed in claim 24 or claim 28.
33. A composition as claimed in claim 31 or claim 32, which is substantially free of water.
34. A composition as claimed in claim 32, made up substantially as any one of those shown in the Table herein, the copolymer powder being substantially as described in any one of Examples I, II, III, IV and V herein.
35. A method of coating a substrate wherein there is used a dispersion powder or composition as claimed in any one of claims 24, 28, and 31 to 34 herein.
36. A method as claimed in claim 35, wherein the substrate is asbestos cement, wood or masonry.

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